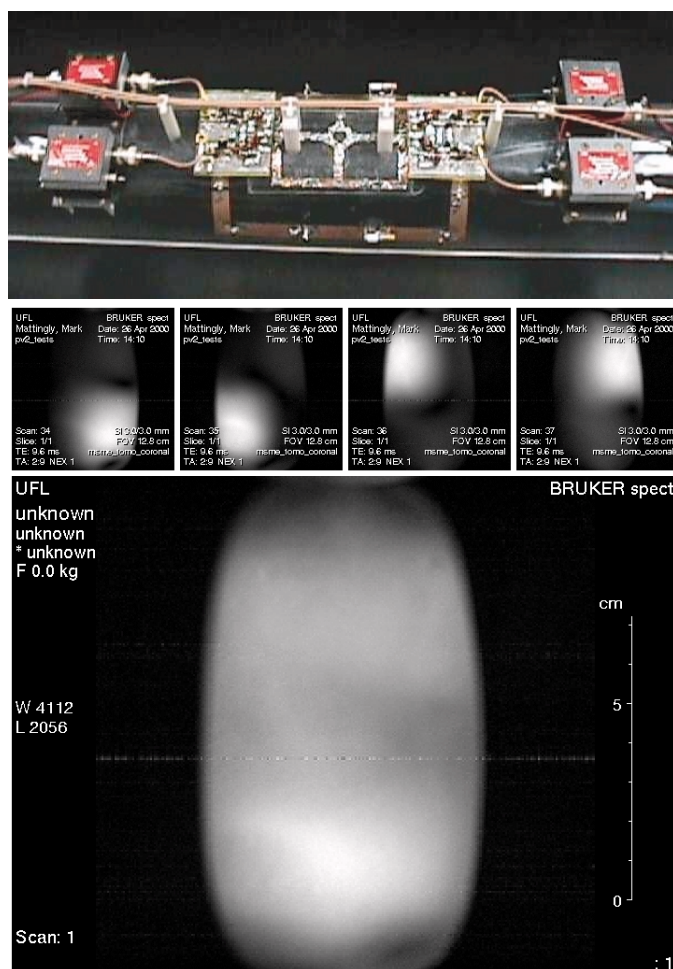


# INSTRUMENTATION

## Development of High Frequency Phased Array Rf Coils

Beck, B.L., UF McKnight Brain Institute/NHMFL  
 Duensing, R., MRI Devices Corporation  
 Fitzsimmons, J., UF McKnight Brain Institute  
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Phased array coils offer improvements in the SNR in imaging and potentially spectroscopy, but so far have been limited to developments on clinical systems at 3 T and below. The goal of this project is to develop phased array coils for the higher field animal



**Figure 1.** Top: 4-coil phased array probe. Bottom: Images from the four separate coils acquired simultaneously (top inserts) can be combined to give one image with a composite field of view (bottom image).

systems in Advanced Magnetic Resonance Imaging and Spectroscopy (AMRIS) Facility. Our 4.7 T, 33 cm system is the first in the United States with phased array capability (4 channel) and the 11.7 T, 40 cm is equipped with similar hardware. At higher fields, phased array also offers potential advantages in circumventing problems arising for the dielectric effect and for reducing the rf power requirements for excitation.

To this end, we have constructed the first phased array coil at 4.7 T (200 MHz). A receive-only 4-channel phased array coil for imaging cat spines was built on an acrylic half cylinder 5 1/2" in diameter. The length and width of the array were chosen to match that of an existing quadrature coil (8 cm wide by 10 cm long). Each loop in the array was 4 cm by 5 cm. Using this coil, the first phased array images at 4.7 T have been collected on a phantom (see Fig. 1). These data have been submitted to a meeting<sup>1</sup> and are being written up for publication. Presently, we are evaluating the performance of the coil on *in vivo* samples and comparing its efficiency to conventional coils.

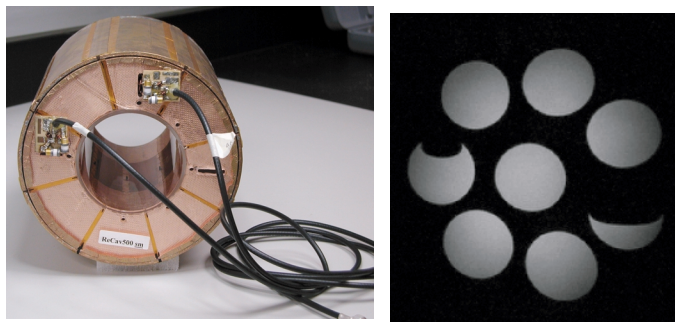
**Acknowledgements:** This work was supported by the NHMFL, the NIH, and the UF McKnight Brain Institute.

<sup>1</sup> Beck, B.L., *et al.*, submitted to ISMRM (2001).

## Development of Large Volume High Frequency RF Coils

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 Blackband, S.J., UF McKnight Brain Institute/UF,  
 Neuroscience/NHMFL  
 Fitzsimmons, J., UF McKnight Brain Institute, UF,  
 Radiology  
 Crozier, S., Univ. of Queensland, Australia, MR  
 Centre

At high frequencies conventional rf coil designs fail, necessitating the development of new coil designs. Last year, we reported the development of a new volume coil design for high frequencies, the



**Figure 1.** 400 MHz ReCav coil (left) and images of a phantom (right).

re-entrant cavity (ReCav) coil, and showed that it was at least as effective as a conventional bird cage coil at 4.7 T, i.e., 200 MHz.<sup>1</sup> This is expected since the birdcage (a few cm in diameter) is effective at that frequency, but becomes problematic at higher frequencies. Thus experiments at higher frequencies were required, and awaited the installation of the 11.7 T/40 cm instrument. Although that instrument is not presently at 11.7 T; it was available for a while at 9.4 T, and thus a ReCav and birdcage coil were constructed for 9.4 T (400 MHz), see Fig. 1.

Using this ReCav and the birdcage coil, images of a phantom at 400 MHz were obtained. The ReCav coil outperformed the birdcage, generating an SNR of 82 vs. 56, and also having a better Q (34 vs. 13). These results are extremely promising and have been submitted to a meeting,<sup>2</sup> with a manuscript in preparation. Since then, two prototype 500 MHz coils have been constructed and bench tested, with the bench test results also indicating good performance. We await the completion of the 11.7 T system to evaluate these coils on real samples. In collaboration with Dr. Crozier in Queensland, Australia, we have also generated simulations of the coil, demonstrating that it behaves more like a cavity than a transmission line array.

**Acknowledgements:** This work gratefully supported by the NHMFL and the UF McKnight Brain Institute.

<sup>1</sup> Beck, *et al.*, Proc. of the ISMRM, Denver, 1388 (2000).

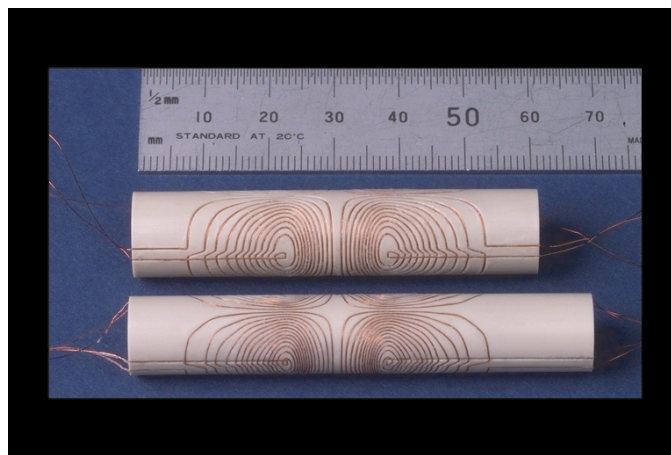
<sup>2</sup> Beck, *et al.*, Submitted to ISMRM (2001).

## Development of Novel Multilayer Transverse Gradient Coils

Bowtell, R., Univ. of Nottingham, England, Physics  
Crozier, S., Univ. of Queensland, Australia, MR Centre  
Beck, B., UF McKnight Brain Institute  
Blackband, S.J., UF McKnight Brain Institute/UF, Neuroscience/NHMFL

Gradient strength is an important criteria in NMR in general, and for MRI studies in a variety of systems. It is important that the NMR signal be dephased/encoded in a time period that is short compared to the NMR characteristic that we wish to measure. For example, sufficient diffusion weighting in MR is critically dependant on the gradient strength so that the echo time is as small as possible. In this way, the SNR is maximized and diffusion times are reduced.

Last year, we described new multilayer gradient coils designed by Dr. Bowtell, and built an axial coil of this design. An axial coil encodes just one spatial direction (z), and so transverse coils (x,y) are also required, but more difficult to fabricate. Although prototype transverse coils have been constructed, the complicated design is hard to fabricate at small sizes. Since that time, Dr. Crozier's team have obtained a new computer controlled lathe with which a working transverse gradient coil has been constructed (Fig. 1). The coil consists of two layers, shown separate in the figure, that are put together coaxially. This coil has been shipped to UF and is being integrated



**Figure 1.** 10 mm diameter transverse multilayer gradient coil.

into a probe for testing on the 750 MHz wide bore instrument.

**Acknowledgements:** This work was supported by the NHMFL, NIH, and the UF McKnight Brain Institute.

## Feedback Stabilization of a High Field Resistive Magnet for NMR

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Schiano, J., The Pennsylvania State Univ., Electrical Engineering

Bredy, E., Universite' Paul Sabatier, France, CNRS

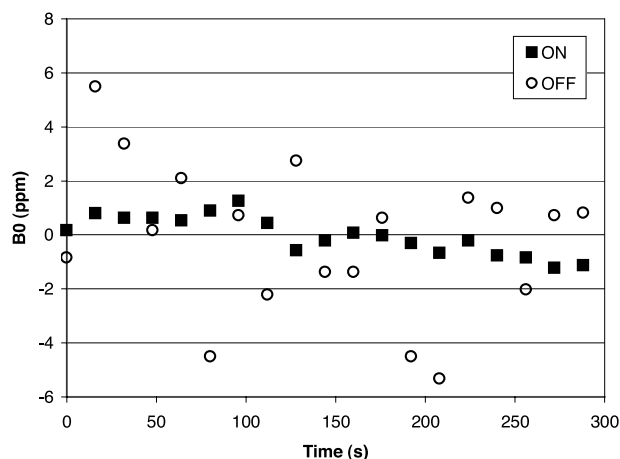
Bird, M.D., NHMFL

Gor'kov, P.L., NHMFL

Powell, J.A., NHMFL

We are developing a 25 T, 52 mm Bitter resistive magnet for NMR applications. Field instability is perhaps the most significant disadvantage of resistive magnets for NMR compared to permanent and superconductive magnets. In particular, a recently proposed resolution-enhancement technique for liquids<sup>1</sup> requires a level of field stability that is significantly greater than that needed for the magnetometry condensed matter NMR applications carried out by the traditional users of high-field, resistive magnets.

Significant improvements to the regulation of the power supply and the cooling water temperature have previously been shown to dramatically decrease ripple and the drift associated with changes in the temperature of the cooling water.<sup>2</sup> Residual noise and drift on the  $\pm 3$  ppm level may more conveniently be corrected with a small solenoidal insert coil. The correction signal for relatively rapid field fluctuations can be detected inductively, in a configuration commonly known as a "flux stabilizer." An effective flux stabilizer makes possible multipulse NMR techniques such as discussed in Ref. 1, and it also reduces high frequency field noise that can confuse an NMR field-frequency lock. At very high fields, the performance of a flux stabilizer can be affected by motion of the pickup coil, whether from the high Lorentz forces on the drive coil or other sources.



**Figure 1.** Time variation of magnetic field  $B_0$  (as measured by NMR) over a period of 5 minutes with the flux stabilizer on and off.

We have studied the power supply noise and flux stabilizer performance and are developing an approach to flux stabilizers that is well-suited to high fields. We have attempted to improve on earlier designs by mechanically isolating the pickup coil from the drive coil, and by matching the size of the pickup coil to size of the sample. The initial results of this approach, shown in Fig. 1, are encouraging. Spectra of a 5 mm diameter sample of Glycine were acquired at intervals of 15 s with the flux stabilizer switched on. The flux stabilizer was then switched off, and the experiment was repeated. Over 300 s, the flux stabilizer reduced the standard deviation in the frequency of the NMR peak from 3 ppm to 0.75 ppm.

<sup>1</sup> Lin, Y.-Y., *et al.*, Phys. Rev. Lett., **85**, 3732 (2000).

<sup>2</sup> Soghomonian, V., *et al.*, Rev. Sci. Instrum., **71**, 2882 (2000).

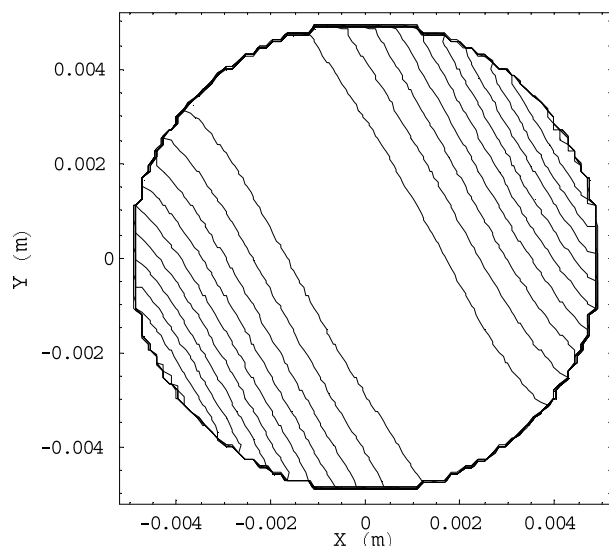
## RF Distortion in High-Field NMR Spectroscopy

Brey, W.W., NHMFL

$B_1$  homogeneity is important to effective solvent suppression and to efficient coherence transfer. Both are critical issues in liquid-state, high-resolution



protein spectroscopy. Degradation of  $B_1$  homogeneity by the sample could offset the gain in sensitivity achieved by using a larger sample. The interaction of electromagnetic fields and human tissue has been extensively studied for MRI applications, and insights based on that effort can be extended to problems in NMR spectroscopy.<sup>1,2</sup>



**Figure 1.** The amplitude of the co-rotating component  $B_{+\omega}(x,y)$  for a 10 mm diameter sample of water with  $\sigma=5$  S/m at 750 MHz. 2% contours are plotted, normalized to the amplitude at the center. The maximum field occurs at  $(x,y)=(0,0)$ .

At the NHMFL, high field, wide bore magnets are available for applications including protein spectroscopy. These range from the 750 MHz, 89 mm bore magnet in Gainesville, to the 1066 MHz, 52 mm bore Keck resistive magnet at the NHMFL in Tallahassee, and the 900 MHz, 100 mm superconductive magnet now under development. It is of interest to evaluate the appropriate sample size for these unique and nearly unique instruments. The RF inhomogeneity across the sample due to the conductivity and dielectric constant of aqueous samples plays a significant role in limiting the possible sample size. An example of the variation of RF field over a large saline sample is shown in Fig. 1.

We have used the effect of the sample contribution to the  $B_1$  inhomogeneity to determine what sample might be appropriate at each field. A typical specification for probe performance is an  $A_{450}$  of 0.85. If only sample-dependent contributions were important, then,

samples up to 10 mm diameter and 5 S/m conductivity would be acceptable at 750 and 900 MHz. At 1066 MHz, samples up to 8 mm and 5 S/m are acceptable, but not the 10 mm samples. Of course, an actual RF coil will add its own contribution to the  $B_1$  inhomogeneity, which must also be taken into account.

It is clear that dielectric resonance and sample conductivity limit effective use of large samples at high fields. Circular polarization has been demonstrated to reduce the effect of tissue loading for clinical MRI. However, the quadrature birdcage coils required have not been successfully applied to NMR spectroscopy. Until new techniques are developed, aqueous samples at high frequency will be limited to small diameter tubes.

<sup>1</sup> Tofts, P.S., J. Magn. Reson. B, **104**, 143-147 (1994).

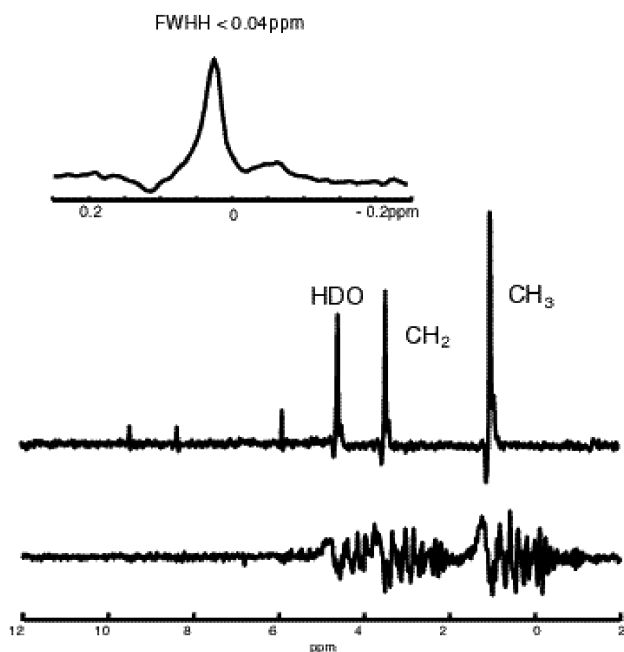
<sup>2</sup> Crozier, S., *et al.*, J. Magn. Reson., **126**, 39-47 (1997).

## HENPEC Approach Toward High Resolution NMR Using the Keck Magnet

Gan, Z., NHMFL  
Murali, N., NHMFL  
Brey, W., NHMFL

Resistive magnets offer magnetic fields higher than superconductive technology, but lack the field homogeneity and stability for high-resolution NMR spectroscopy. An approach named HENPEC has been developed to correct severe magnetic field fluctuations. The HEteroNuclear PhasE Correction method is based on the fact that magnetic field fluctuations perturb only the instant phase of the time-domain NMR signals. The phase effect can be measured from the reference solvent recorded simultaneously with the desired NMR signal. The effects of field fluctuations to the desired signal can then be corrected by a multiplication of the extracted phase factors. This approach corrects both the slow field drift and the fast field fluctuations.

Fig. 1 shows the ethanol proton NMR spectrum recorded on the Keck magnet at the NHMFL. The HENPEC spectrum was acquired using a Tecmag



**Figure 1.**  $^1\text{H}$  spectra of  $\text{CH}_3\text{CH}_2\text{OH}/\text{D}_2\text{O}$  with (middle) and without (bottom) HENPEC.

console modified for two-channel ( $^1\text{H}$  and  $^2\text{H}$ ) data acquisition. The magnetic field inhomogeneity was reduced by magic-angle sample spinning and restricting the sample volume to a 4 mm sphere. The correction of field fluctuation leads to a  $^1\text{H}$  line width, about 40 ppb, an order of magnitude improvement on the best line width ever recorded on the Keck magnet. The 40 ppb line width is approaching the minimum requirement of high-resolution solution NMR spectroscopy. The 25 T field strength and high-resolution capability of the Keck magnet provide an unique opportunity to study field-dependent NMR phenomena, such as the TROSY effect that could push up the size limitation of structure characterization by NMR spectroscopy.

## Milestones in Fourier Transform Ion Cyclotron Resonance Mass Spectrometry Technique Development

Marshall, A.G., NHMFL/FSU, Chemistry

The present range and power of Fourier transform ion cyclotron resonance mass spectrometry rest on a number of prior technique developments. In Ref. 1,

selected developments in neutral/ion introduction, ionization methods, excitation/detection, ion trap configuration/operating modes, ion dissociation and MS/MS, ion cooling techniques, theory, and data reduction are briefly explained and chronicled. Evidence for the value of these techniques is provided by a compilation of current world records for mass resolution, mass resolving power, and mass accuracy. With these capabilities, it becomes possible to resolve and identify up to thousands of components of a complex mixture, often without prior wet chemical separation, thereby potentially changing the whole approach to dealing with chemical and biological complexity.

**Table 1.** FT-ICR world records for mass analysis (\* denotes record held by NHMFL personnel and/or spectrometers).

### Mass accuracy/Elemental composition

1. Highest mass accuracy over wide mass range:  **$\pm 0.5$  ppm from 90-300 Da\***  
 **$\pm 1$  ppm from 250-1000 Da\***
2. Highest mass for unique elemental composition: **895 Da\***
3. Highest mass precision:  **$\pm 0.000\,000\,09$  Da @ 20 Da\***

### Mass resolving power, $m/\Delta m_{50\%}$

1. Highest resolving power for ions of a single  $m/z$ : **200,000,000**
2. Highest resolving power for ions of multiple  $m/z$  at high mass: **8,000,000 @ 8.6 kDa\***

### Mass resolution (separation of closely-spaced masses)

1. Highest resolution of two molecules: **0.00045 Da @ 906 Da\***
2. Highest direct-mode (broadband resolution): **0.0034 Da @ 1326 Da\***
3. Highest mass for resolved isotopic fine structure: **15.8 kDa\***
4. Highest mass for unit mass resolution: **112 kDa\***

### Most complex mixture analyzed from a single mass spectrum

1.  **$\sim 5,000$  elemental compositions\***
2. **583 peptides**, resolved to better than 1 Da\*

**Highest mass** for a chemically pure molecule:  
**100,000,000 Da.**

### Tandem mass spectrometry

1. Highest mass resolving power for MS<sup>1</sup>:  
**20,000\***
2. Highest mass resolving power for MS<sup>2</sup>:  
Similar to FT-ICR without MS<sup>1</sup>.\*

**Acknowledgements:** This work was supported by NSF (CHE-99-09502), NIH (GM/RR-31683), FSU, and the NHMFL.

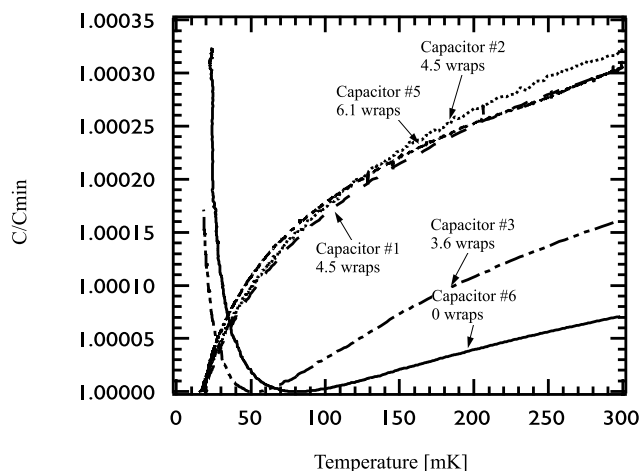
<sup>1</sup> Marshall, A.G., "Milestones in Fourier Transform Ion Cyclotron Resonance Mass Spectrometry Technique Development," *Int. J. Mass Spectrom.*, **200**, 331-356 (2000).

## Thermometry at Low Temperatures in High Magnetic Fields

Palm, E.C., NHMFL  
Murphy, T.P., NHMFL  
Hannahs, S.T., NHMFL  
Tozer, S.W., NHMFL  
Hall, D., NHMFL  
Kauppinen, J.P., Nanoway Oy, Finland

Conventional resistance thermometers have significant magnetoresistance when used at low temperatures and high magnetic fields which makes the accurate determination of temperature problematic. Therefore, we have continued our pursuit of alternate devices for practical thermometry in this temperature/field region. We have continued to improve our capacitance thermometer fabricated from thin layers of kapton and copper held together with Stycast 1266 epoxy. By changing the construction parameters of these devices, we have demonstrated that we can change their sensitivity to temperature and move the minimum that occurs in the capacitance-temperature trace to lower temperatures (see Fig. 1). In addition, their dependence upon frequency and excitation was mapped out. A paper has been submitted to RSI on this work.

We have also continued our collaboration with Nanoway Oy on their nanofabricated Coulomb



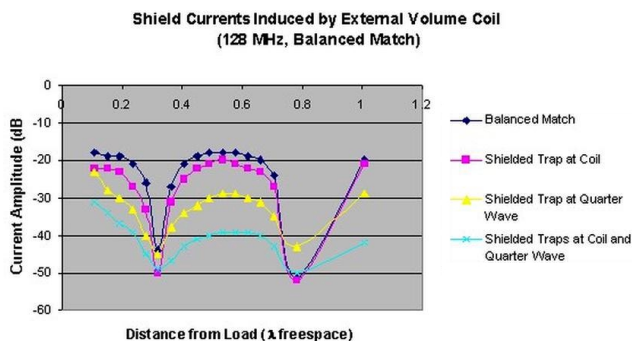
**Figure 1.** Capacitance vs. temperature for a number of devices with different construction parameters.

blockade thermometers (CBTs). Preliminary studies on CBT devices optimized for temperatures above 1 K were performed. These studies were performed in liquid helium using vapor pressure to assure the temperature of the devices remained constant. These studies indicated that the device was field insensitive in secondary mode to less than 0.1% at fields up to 31 T. In the future, the low temperature version of these devices will be measured at temperatures down to 50 mK and fields to 33 T.

## Reduction of Cable Shield Currents Generated by External Volume Coils

Peterson, D., UF, Radiology/MRI Devices Corporation  
Beck, B., NHMFL/UF McKnight Brain Institute  
Duensing, R., MRI Devices Corporation

In the cables used to connect rf coils to the NMR console, currents can flow on the shield of a coaxial cable, apart from the signal current flowing on the center conductor of the cable. These currents may be generated by the local transmit/receive coil, or by the surrounding transmit coil. We have demonstrated<sup>1</sup> that the use of balanced matching schemes and cable traps can reduce shield currents if the local coil is considered the source. This work has been further developed to focus on the measurement and reduction of shield currents that are induced by a surrounding volume coil, and builds on the work



**Figure 1.** Shield currents on cable of coil with balanced match (128 MHz).

previously described to bring a greater understanding to this area of RF coil design.<sup>2</sup>

We have shown that matching schemes on the local coil are ineffective in suppressing shield currents caused by an external source. The designer must rely on other methods to suppress such currents, such as cable traps. Fig. 1 shows the effectiveness of the cable trap on balanced matched coils, and are as effective when the coil is unbalanced match. Our model of shield currents that is very simple and controlled, and does not reflect the exact cable environment of an MR exam. The placement of the cable near patient bodies or the side of the bore will affect the pattern the shield currents will take. The optimum placement of cable traps is one that should be examined in the particular cable environment of interest. As NMR/MRI moves to higher and higher field strengths and larger bore sizes, great care must be taken in the engineering design of the RF coil to ensure reduction of electric fields, cable shield currents, and other radiative losses.

**Acknowledgements:** This work was supported by the NHMFL, and the UF McKnight Brain Institute.

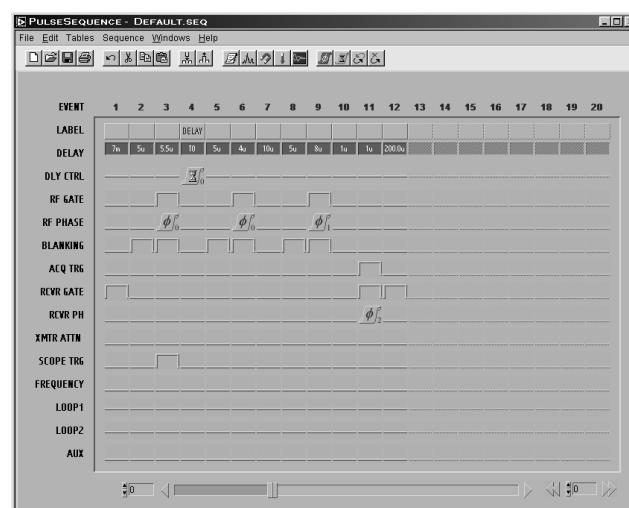
- <sup>1</sup> Beck, B.L., *et al.*, Proc ISMRM, Denver (2000).
- <sup>2</sup> Beck, B., *et al.*, Submitted to ISMRM (2001).

## A 2GHz NMR Spectrometer

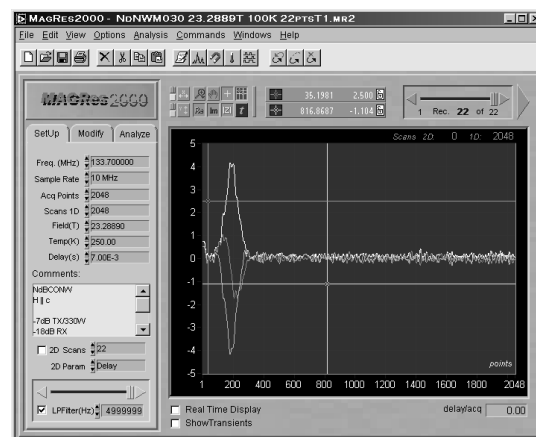
■ IHRP ■

Reyes, A.P., NHMFL

The Condensed Matter NMR Group has designed, built and tested a versatile NMR spectrometer capable of transmitting and receiving RF signals over a broad frequency range—2 MHz to 2 GHz. The all-in-one design integrates all the I/O and data acquisition functions into a computer by using commercially available hardware modules. This concept allows unlimited flexibility in spectrometer functionality by placing control of key components completely on software. Using computer expansion cards also allows huge reduction in cost while enhancing speed and reliability—data transfers are limited only by the bus speed, and the communication delays that are associated with stand-alone equipment are



**Figure 1.** Pulse-sequencer user interface.



**Figure 2.** Data acquisition user interface.

eliminated. RF pulse widths as short as 20 ns and data transfers as fast as 133 MBps are possible. Digitizing rate can be as fast as 50 MS/s on two channels and RF phase rotation can be accomplished in  $0.36^\circ$  increments. Using a quadrature homodyne detection method improves the signal-to-noise ratio since all signal processing (filtering, phase shifting, gain, etc) is accomplished at baseband. The receiver dead time after an RF pulse is about 2  $\mu$ s at 500 MHz.

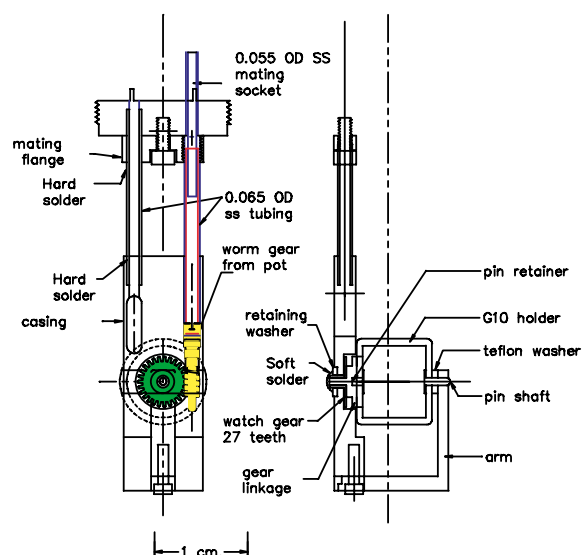
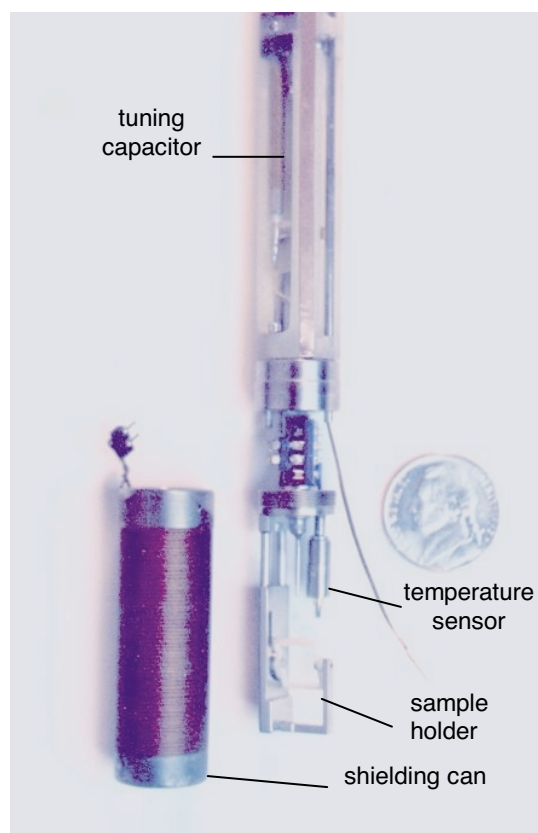
The spectrometer interface was designed and built at the laboratory, and it utilizes a graphical user interface for both pulse programming and data acquisition.<sup>1</sup> Completely software driven, the pulse sequencer emulates real-world knobs and switches to provide real-time delay and frequency controls. Complicated pulse sequences can be programmed, including delay and phase tables, and real-time frequency shifting. In an effort to improve efficiency of data taking and maximize the productivity during valuable magnet time, the software also includes full automation of temperature, frequency and field sweeps as well as user flexibility in programming arduous and time consuming tasks through the use of scripts. Other capabilities include sophisticated data reduction and analysis, e.g. digital filtering, baseline correction, Fourier transform, apodization, windowing, phase shifting, integration, moment analysis, FFT series-sum, and non-linear squares fit—all in one software package.

<sup>1</sup> For details, browse <http://vortex.magnet.fsu.edu/cmpnmr/>

## A Cryogenic NMR Goniometer for 32 mm Resistive Magnets ■ IHRP ■

Reyes, A.P., NHMFL

The small bores of the high field Bitter magnets have put enormous constraints on the design of NMR probes.<sup>1</sup> The restriction is often aggravated by the need to install cryogenic equipment for low temperature condensed matter physics experiments. Although some of the problems have been solved, as with regards to the helium bubble and capacitor breakdown in the RF circuit,<sup>1</sup> the price for these



**Figure 1.** Bottom of probe showing the goniometer (with a rectangular sample holder, center). The gears are hidden inside a casing. The barrel at left is a shielding can with heater wires wrapped around it and which protects the goniometer. Dangling wires are for temperature and hall sensor. Tuning capacitors can be seen mounted above. Schematic showing details of construction is shown below.



innovations is a yet smaller sample volume. If one desires to increase the parameter space, e.g., orientation, a design has to involve much creativity to take advantage of the unused space in the magnet without sacrificing much for the sample.

The Condensed Matter NMR group at the NHMFL has designed and constructed a remotely accessed goniometer to fit the severely constrained environment in the Bitter magnet (Fig. 1). With the exception of the sample holder, the 12 mm diameter device is an all-(non-magnetic) metal construction to reduce errors due to thermal expansion. The miniature gears are extracted from antique (metal) mechanical watches and commercial trim potentiometers. The device is fully demountable at the bottom of the NMR probe and is capable of accommodating samples of up to 5 mm diameter x 7 mm length. Using flexible leads to feed the NMR coil, a full 360° sample rotation is possible. Orientation feedback is provided by a calibrated knob at the top of the probe as well as electrical signals from the Hall sensors mounted on the sample holder. The mechanical resolution is 0.2°.

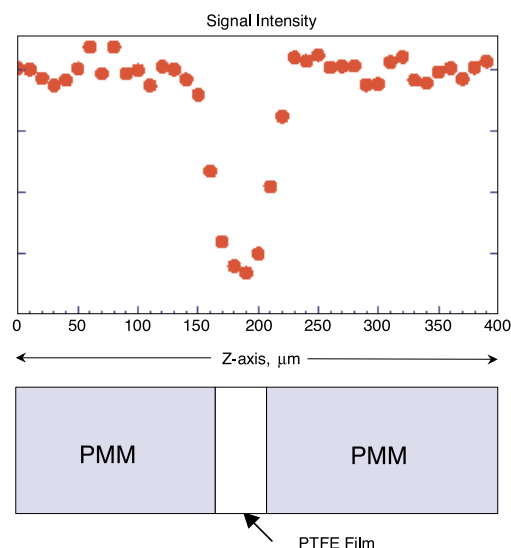
**Acknowledgements:** This work performed in collaboration with P. L. Kuhns and W. G. Moulton.

<sup>1</sup> Reyes, A.P., *et al.*, Rev. Sci. Instrum., **68**, 2132 (1997).

## A New STRAFI System for the 833 MHz NMR Spectrometer

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Russian Academy of Sciences  
Brey, W.W., NHMFL  
Gor'kov, P.L., NHMFL  
Fu, R., NHMFL

The stray field imaging (STRAFI) technique<sup>1</sup> is a powerful method for the determination of the distribution of spin density and relaxation time in solids. It was found that the high field gradients at the end of small bore, high field superconducting solenoids can be used to create high spatial resolution spin density profiles even for samples with very



**Figure 1.** 1D image of resolution sample.

rapid relaxation.<sup>2,3</sup> The 19.6 T, 32 mm bore superconductive magnet has an enormous field gradient that is particularly suitable for STRAFI. The maximum static gradient of 75 T/m is developed at a field of about 11.7 T. The high gradient enables excellent resolution, and the high field improves sensitivity, which is especially important for imaging non-proton nuclei.

We have developed a STRAFI system for this magnet which can be used to obtain high resolution 1D images of layered structures. The system is based on a stepper-motor driven Resonance Research NMR field mapping system linked to a Tecmag, Inc, NMR spectrometer. The probehead consists of a static part fixed to the magnet shim system and a moving part containing an Alderman-Grant coil (12 mm i.d. and 20 mm window). The coil was tuned to 520 MHz (12.2 T for protons). The uniform RF field range is estimated to be 14 mm along the gradient direction.

To explore the performance of the new system, a test sample was made consisting of two Poly (methyl methacrylate) disks (10 mm dia., 5 mm thick) separated by a proton-free 39 micron PTFE film. The sample spin density profile, measured as the echo intensity vs. the sample displacement, is depicted in Fig. 1. That result shows an ultimate spatial resolution of least of the same value as the PTFE film thickness.

- <sup>1</sup> McDonald, P.J., *Progress in NMR Spectroscopy*, **30**, 69 (1997).
- <sup>2</sup> Samoilenko, A.A., *et al.*, *JEPT Lett.*, **47**, 348 (1988).
- <sup>3</sup> Randall, E.W., *et al.*, *J. Magn. Reson. A*, **116**, 122 (1995).

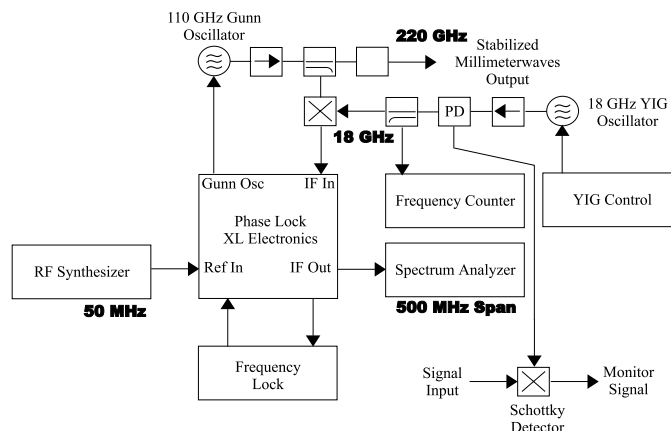
## Source Stabilization and Control for High-Frequency EMR Spectroscopy

Saylor, C.A., NHMFL  
 Maresch, G.G., NHMFL  
 Brunel, L.-C., NHMFL

The noise level of an electron paramagnetic resonance (EPR) spectrum is partially determined by the frequency and phase noise of the microwave source. Conventional EPR spectrometers use external cavity stabilization and automatic frequency control (AFC) circuits to achieve optimum sensitivity. For the NHMFL high- and multi-frequency (HFEPR) spectrometer, cavities do not provide sufficient stability for optimum noise suppression. Operating at frequencies above 100 GHz, phase locking circuits to lower the frequency reference oscillators are needed for optimum performance.

A millimeter-wave vector analyzer can be used for phase locking the microwave source that are Gunn diode oscillators. Currently Gunn sources are in use which provide frequencies at 95 GHz and 110 GHz. Yttrium iron garnet (YIG) oscillators operate as low-frequency references for phase locking the millimeter-wave Gunn diodes.

For the improvement of amplitude, frequency, and phase stability of the HFEPR spectrometer, a new locking circuit has been constructed as a replacement for the millimeter-wave vector analyzer. The millimeter-wave Gunn oscillator is controlled by an XL phase lock electronic unit, which itself is locked to a 50 MHz reference signal produced by a radio frequency (RF) synthesizer. As an intermediate frequency source, a 18 GHz YIG oscillator is used. In addition, the YIG signal is split by a power divider (PD), which provides a reference signal to the Schottky detector for the generation of a monitor signal. This monitor signal can be used for microwave adjustments before measurement, or for direct, non field modulated detection of the EPR



**Figure 1.** Schematic view of the source locking electronics for high frequency EPR spectroscopy, e.g., for 220 GHz resonance frequency.

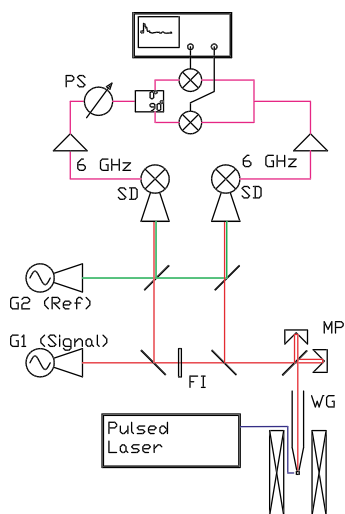
signal. As a result of the new frequency and phase lock electronics, in EPR experiments at 220 GHz, a signal-to-noise improvement of better than 30% could be measured. This directly corresponds to a sensitivity enhancement of the instrument.

**Acknowledgements:** This work was supported by NSF grant 5024-54522.

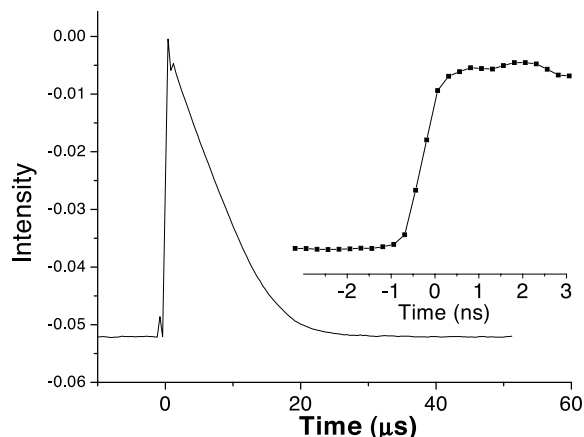
## A High Field Transient Electron Magnetic Resonance Spectrometer

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 Brunel, L.-C., NHMFL

The inherent timescale of an electron magnetic resonance (EMR) experiment is inversely proportional to the measurement frequency, and allows faster measurements at higher frequencies. In time-resolved EPR, this enables the measurement of systems with very short lifetimes and/or fast relaxation rates, and this prompted the construction of a new high field spectrometer with both fast detection and optical access for excitation of paramagnetic excited states and/or creation of paramagnetic reaction intermediates. The design of the spectrometer, which operates at 120, 240, and 360 GHz, combines quasi-optical techniques and a super-heterodyne detection scheme based on Schottky diode mixers (see Fig. 1). It features both sub-ns time-resolution and a high g-resolution. The room temperature sensitivity



**Figure 1.** Schematic layout of the transient superheterodyne EPR spectrometer. G1 is the signal Gunn diode phase-locked source operating at 120, 240, or 360 GHz. The reference oscillator G2 is tuned to 6 GHz below that. FI: Ferrite Isolator. MP: Martin-Pupplet serving as polarization converter. WG: Corrugated oversized waveguide. SD: Schottky diode mixer. The 6 GHz IF signals are amplified and mixed down to 0 to 2 GHz, and recorded with a 1.5 GHz digital oscilloscope.



**Figure 2.** Measured response of Si-wafer transmission at 240 GHz to a 120 ps laser pulse (532 nm) at room temperature.

in CW-mode is of the order of  $10^{11}$  spins/gauss without cavity and  $5 \times 10^8$  spins/gauss in a Fabry-Perot cavity.

The time resolution was measured with a high-purity Si-wafer placed in the beam path close to the Brewster angle. Illumination with a high-power laser pulse above the band gap creates an electron-hole plasma on the surface of the semiconductor, which reduces the transmission significantly. The decrease of the transmission in response to a 110 ps laser pulse was measured in the EMR setup to be 600 ps (95% to 5% transmission). The decay to equilibrium is much

slower and corresponds to three processes: Auger recombination, radiative recombination, and impurity recombination. In our Si-wafer, this recombination is of the order of 20 microseconds at room temperature. The laser pulse intensity was about  $30 \text{ mJ/cm}^2$  at a wavelength of 532 nm.

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## Triple Resonance Microcoils for High Field NMR ▀IHRP▴

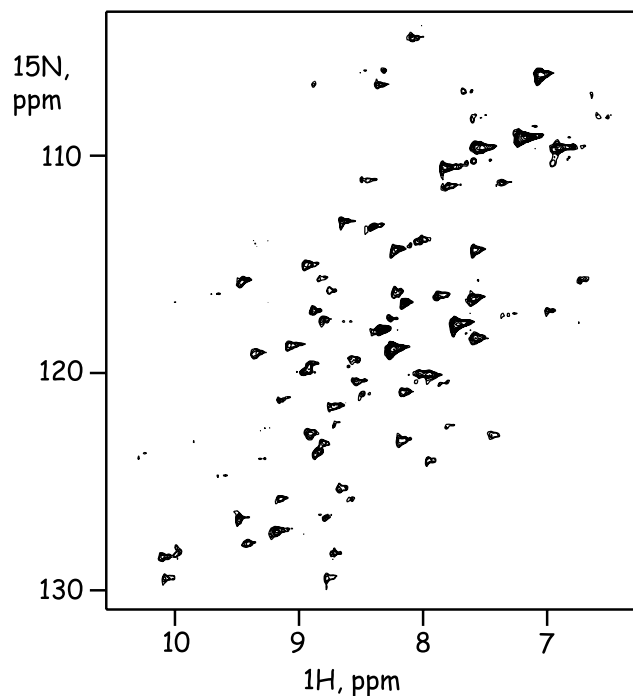
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Microcoils have recently been introduced into the high resolution NMR community. The main advantages of microcoil rf probe are the small size and the increased rf coupling arising to the high filling factor. This improved filling factor provides significantly higher sensitivity for mass-limited samples with substantially shorter  $90^\circ$  pulse widths. Mass-limited samples arise when investigating post-translational modifications in eukaryotic systems, for example glycosylation. The shorter  $90^\circ$  pulse widths provide more uniform spectral bandwidth coverage and more efficient decoupling at high magnetic fields. The small size suggests that these coils may allow high resolution spectroscopy in high field, moderate homogeneity magnets like the Keck and the 833 MHz system. However, these microcoils have only previously been demonstrated for  $^1\text{H}$  and  $^1\text{H}/^{13}\text{C}$  tuned circuits applied to small molecules. There are significant questions relating to the utility of microcoils for high-resolution structural biology research. The primary aim of this research is to design and construct microcoils that could be used to determine the structures of biological macromolecules. This would require a triple-resonance coil, with pulsed field gradient accessories. In the past year, we have made significant progress towards this goal.



**Figure 1.**  $^2\text{H}$   $^1\text{H}$ ,  $^{15}\text{N}$  correlation spectrum of FK506 binding protein collected in ~16 hours accumulation. SNR on isolated resonances is approximately 3:1. The total amount of protein in the active region of the coil was 10  $\mu\text{g}$ .

Our initial focus is to optimize a  $^1\text{H}$ ,  $^{15}\text{N}$  doubly-tuned microcoil probe. Our best microcoil to date was wound using 4 turns of 26 AWG round wire spaced by 30 AWG wire, for a total length of 3 mm, with the components optimized for  $^1\text{H}$  sensitivity. This probe had significantly improved  $^1\text{H}$  performance with somewhat degraded  $^{15}\text{N}$  performance (90° pulse width ~3 ms and 45 ms for  $^1\text{H}$  and  $^{15}\text{N}$ , respectively, compared to earlier versions of the probe that had different numbers of coils and or used different wire. Fig.1 shows a 2D HSQC spectrum collected on a ~1 mM FKBP sample in 16 hours using this coil, which shows adequate sensitivity given the preliminary stage of the project. The poor lineshape probably results from incomplete decoupling in the observed dimension. These decoupling parameters were difficult to measure accurately due to very weak signal at low rf powers. We are currently focusing on optimizing rf homogeneity. After completion of the next round of development, we will turn our efforts to introducing triple-resonance capabilities. Our initial design will be to develop a doubly-tuned inner coil ( $^1\text{H}/^2\text{H}$ ) coupled with an outer coil to provide  $^{13}\text{C}/^{15}\text{N}$  rf pulses.

## A High-Field NMR Magnetometer That Uses Flowing Water

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An NMR magnetometer using pre-polarized flowing water has been designed and test measurements have been made at the NHMFL. The flowing design has the advantage of high precision and low requirement on field homogeneity.<sup>1,2</sup> The magnetometer has a measuring range from 0.01 Gauss to 20 T or even higher.

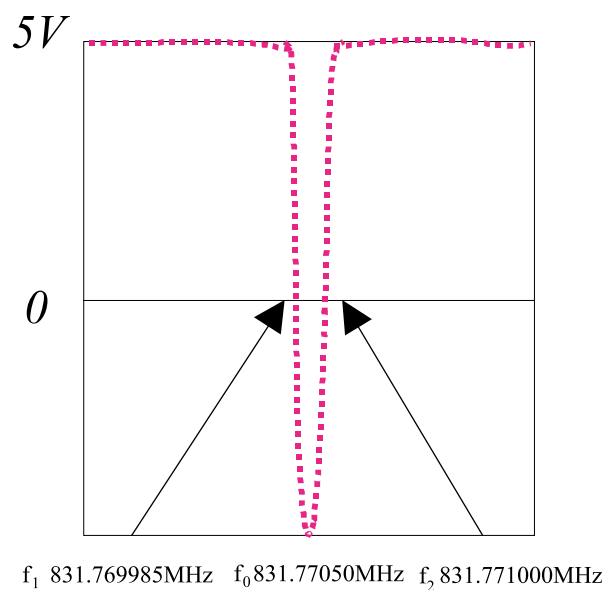


**Figure 1.** Indication signal of NMR analyzer.

The magnetometer probe is cylindrical (16 mm diameter, 140 mm in length) connected with 5-meter flexible cable. Prepolarized water is pumped into the probe continuously using a high-pressure micro-pump mounted inside the instrument case. The NMR analyzer converts proton polarization of the flowing water into electronic indication signal (Fig. 1). When the RF frequency sweeps through the Larmor frequency at the measured field strength, the electronic signal will be flopped and inverted, which indicates the occurrence of resonance. Fig. 2, shows the signal occurred when the RF irradiation sweeps through the center field of the 19.6 T superconductive magnet at the NHMFL.

For determination of center resonance frequency, one can measure the frequency  $f_1$  and  $f_2$  at two half-





**Figure 2.** Absorption line at 19.6 T field.

height points of the resonance absorption line (Fig. 2). Maximum sensitivity of signal amplitude vs. frequency variation exists at these two points. The average of  $f_1$  and  $f_2$  gives the measured field strength with high precision.

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<sup>1</sup> Pendlebury, J.M., *et al.*, Rev. Sci. Instr., **50**, 535-540 (1979).

<sup>2</sup> Ye, S., J. Appl. Phys., **57**, 3830 (1985).

